

Experimental Evidence for a Shape Resonance in Acetylene

The identification of elusive spectroscopic features known as shape resonances, once touted as a tool for measuring molecular bond lengths, has over the years proven to be controversial. Now, symmetry-resolved photoelectron spectroscopy measurements taken at the ALS have provided the first convincing evidence for the existence of a shape resonance in acetylene that was originally proposed for this molecule 15 years ago.

In photoelectron emission from molecules, shape resonances occur when photoelectrons are temporarily trapped by a potential energy barrier in the molecule. As the name suggests, this effect depends upon the shape of the electron's potential energy well, which in turn depends upon the configuration of the molecule. It was thus initially thought that shape resonances might be a simple way to obtain information about molecular geometry. In particular, it was thought that the energy at which a shape resonance occurred could be

correlated with the length of molecular bonds.

An attempt was made 15 years ago to quantify the relationship between shape-resonance energy and bond length for a number of small molecules with low-*z* elements, including acetylene. However, shape resonances are manifested as broad (and thus, somewhat ambiguous) peaks in the photoelectron cross section as a function of photon energy, and the criteria for identifying shape resonances in general were unclear. Subsequent studies of key molecules that have obvious variations in bond lengths found only weak evidence for a shape resonance in acetylene.

The high brightness of the ALS photon beam and the high resolution afforded by Beamline 10.0.1 (formerly 9.0.1) allowed T.D. Thomas of Oregon State University and his colleagues to see features of the photoelectron spectrum that were not readily apparent in previous work. With the ALS data, the

researchers were able to resolve the symmetry splitting of the carbon 1s peak of acetylene. This splitting arises when the core 1s orbitals of the two carbon atoms in acetylene (HCCH) combine to produce two closely spaced molecular orbitals, designated " $1\sigma_g$ " and " $1\sigma_u$." The symmetry of the orbital wave function is designated by the letters *g* (*gerade*—symmetric) and *u* (*ungerade*—antisymmetric).

This symmetry resolution is crucial because, according to dipole selection rules, transitions to the shape resonance can result only from $1\sigma_g$ ionization. Thus, the observation of enhanced $1\sigma_g$ ionization (i.e., larger $1\sigma_g$ cross section) at the predicted energy would provide strong support for the existence of a shape resonance.

Thomas et al. compared the $1\sigma_u$ and $1\sigma_g$ ionization cross sections by plotting the ratio of the $1\sigma_u/1\sigma_g$ cross sections vs. incident photon energy. The ratio goes through a minimum (i.e., the $1\sigma_g$ cross section is at a maximum) at a photon

energy of about 317 eV. This energy coincides with the location of the shape resonance indicated by previous investigations and is slightly higher than that predicted by theory. These results also provide a test of theoretical calculations of the photoionization cross section near the photoionization threshold for both *u* and *g* ionization. The researchers found that the theory successfully reproduces the trend of the data, indicating that most of the basic physics has been included.

Although prospects for the original "molecular bond ruler" concept appear to be dim because of the difficulty involved in identifying shape resonances and because of the complexity of the correlation (if any), this result clearly demonstrates how the improvements in spectral resolution made possible by the ALS can help resolve outstanding questions in the scientific literature and lead to better understanding of the inner workings of molecules.

T.D. Thomas (541-737-6711), Department of Chemistry, Oregon State University.

T.D. Thomas, N. Berrah, J. Bozek, T.X. Carroll, J. Hahne, T. Karlsen, E. Kukk, L.J. Saethre, "Photon Energy Dependence of the $1\sigma_u/1\sigma_g$ Intensity Ratio in Carbon 1s Photoelectron Spectroscopy of Ethyne," *Phys. Rev. Lett.* **82** (1999) 1120.

RESEARCH FUNDING: Divisions of Chemical (DCS) and Materials Sciences (DMS), U. S. Department of Energy; National Science Foundation; Research Council of Norway. Operation of the ALS is supported by DMS.



SYMMETRY-RESOLVED PHOTOELECTRON SPECTROSCOPY



Experimental Evidence for a Shape Resonance in Acetylene

- **Shape resonances**

- *Photoelectrons are temporarily trapped by molecular potential barrier*
- *Proposed as “molecular bond ruler” 15 years ago*

- **Unclear criteria for identifying shape resonances**

- *Broad, ambiguous peaks in photoelectron cross section*
- *Ambiguous experimental evidence*

- **Splitting of energy levels in acetylene (HCCH)**

- *Core atomic orbitals ($1s$) combine to form two molecular orbitals (MOs)*
- *MO wave functions are symmetric ($1\sigma_g$) or antisymmetric ($1\sigma_u$)*
- *Enhanced $1\sigma_g$ ionization is a strong indicator of shape resonance*

- **Resolution of question at ALS**

- *Resolve symmetry splitting in molecular energy levels (~ 100 meV)*
- *Obtain convincing evidence of shape resonance in acetylene*
- *Test theoretical calculations of the photoionization cross section*

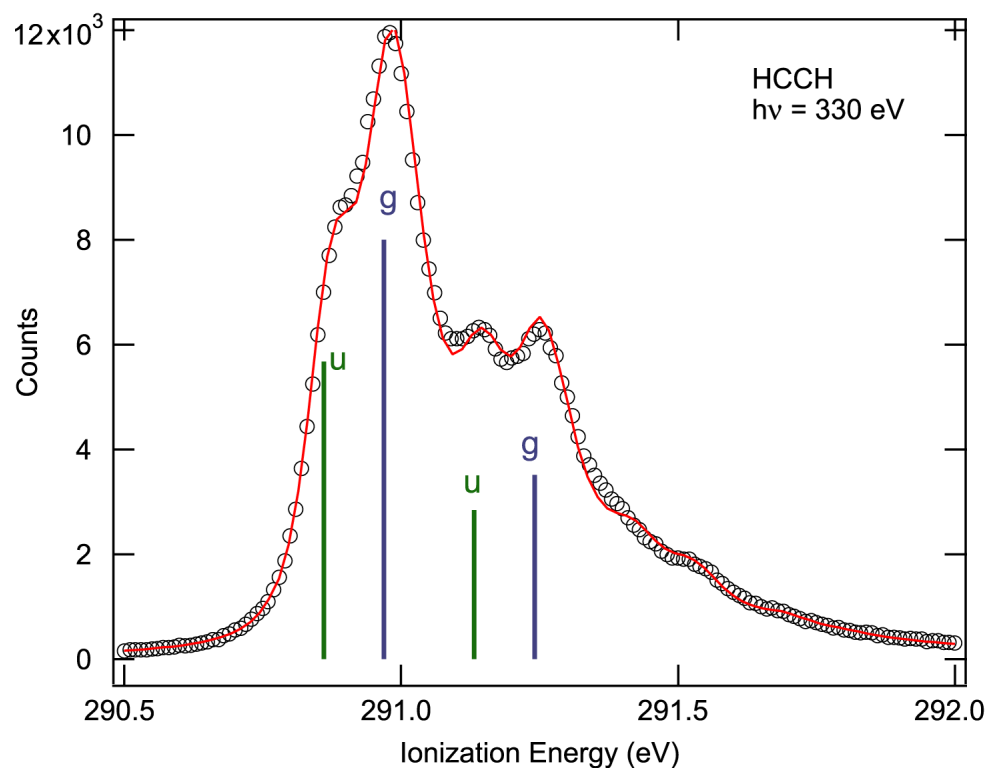


SYMMETRY-RESOLVED PHOTOELECTRON SPECTROSCOPY



Experimental Evidence for a Shape Resonance in Acetylene

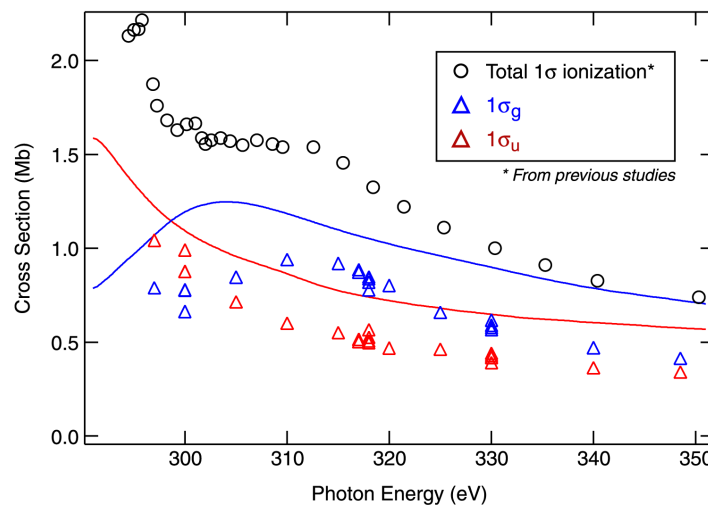
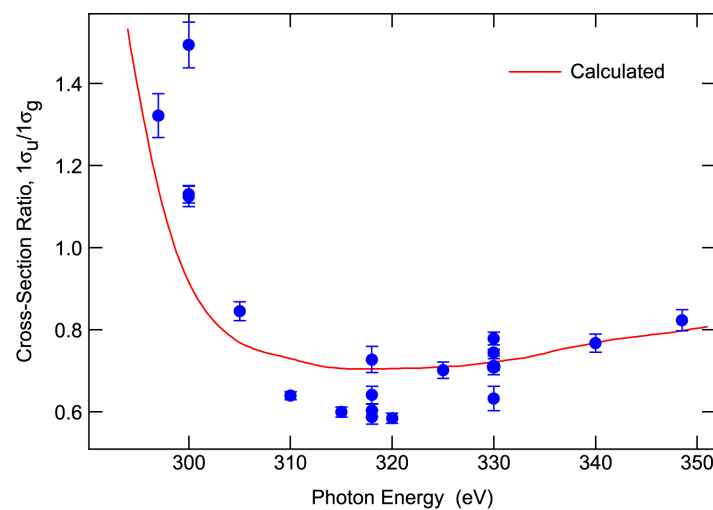
Carbon 1s Photoelectron Spectra of Acetylene



Symmetry-resolved ALS measurements show relative intensities of $1\sigma_u$ and $1\sigma_g$ ionization.

Experimental Evidence for a Shape Resonance in Acetylene

$1\sigma_u/1\sigma_g$ vs. photon energy goes through a minimum (i.e., $1\sigma_g$ is at a maximum) at ~317 eV.



Comparison of experimental (△) and calculated (solid lines) $1\sigma_g$ and $1\sigma_u$ cross sections.